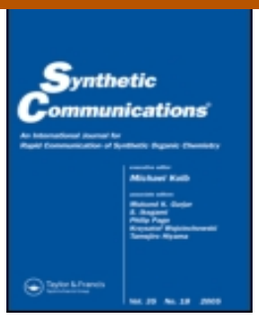

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Synthesis of N_1 and N_2 coumarin substituted 1,2,3-triazole isomers via click chemistry approach

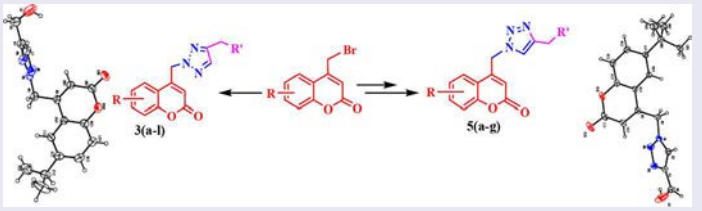
Devadas Shamala[a], Kalegowda Shivashankar[a], Chandra[b], and Madegowda Mahendra[b]

[a]P.G. Department of Chemistry, Central College Campus, Bangalore University, Bangalore, Karnataka, India; [b]Department of Studies in Physics, Manasagangotri, University of Mysore, Mysore, Karnataka, India

ABSTRACT

The synthesis of N_1 and N_2 coumarin substituted 1,2,3-triazole isomers from terminal alkynes, sodium azide, and 4-bromomethylcoumarins in the presence of triethylamine as a base and CuI as a catalyst in good yield are reported. The molecular structure of compounds **3g** and **5d** are established by single-crystal analysis.

GRAPHICAL ABSTRACT



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KEYWORDS
Azide; 4-bromomethylcoumarins; click chemistry; copper iodide; coumarins; triazoles

Introduction

Sharpless established the concept of click chemistry, which has been exploited as a powerful tool for the development and discovery of drugs. A click reaction consists of readily available reactants and reagents as well as simple reaction conditions and purification process. Click reactions must furnish good yields and stable products under physiological conditions. Of the reactions in the click universe, the perfect example is the Huisgen 1,3-dipolar cycloaddition of alkynes to azides to form N_1 substituted 1,2,3-triazoles.[1]

The synthesis of 1,2,3-triazoles is an important synthetic reaction as these scaffolds are found to form a very important core in numerous synthetic, pharmaceuticals, and a wide variety of biologically active compounds.[2] A large number of compounds bearing 1,2,3-triazole scaffolds have entered preclinical and clinical trials over the past few years. Some commercially available 1,2,3-triazole drugs[3] (Fig. 1) including bazel (antiepileptic drug), tazocin ef (antibiotic for community-acquired pneumonia caused by *Pseudomonas aeruginosa*), and suvorexant (brain penetrant dual orexin receptor antagonist) are derived from

CONTACT K. Shivashankar shivashankark@gmail.com P.G. Department of Chemistry, Central College Campus, Bangalore University, Bangalore 560 001, Karnataka, India.
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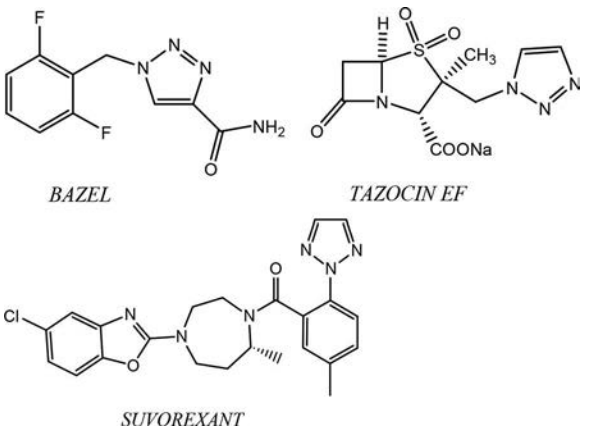


Figure 1. Commercially available triazole drugs.

triazole core entities. 1,2,3-Triazole structure moieties also exhibited antibacterial,[4] antiprotozoal,[5] antifungal,[6] antioxidant,[7] antitubercular,[8] and anticancer[9] activities. Coumarins are known to be biologically versatile compounds possessing several biological properties.[10] It has been reported that coumarin compounds bearing other heterocyclic systems possess a number of interesting biological activities such as antitumor,[11] antioxidant,[12] anti-ischemic,[13] and anticancer[14] activities. Based on the survey of recent literature studies on triazoles and coumarins, the aim of our work is synthesis of triazolylcoumarins.

The synthesis of 1,2,3-triazoles has evoked much attention, and a variety of synthetic methodologies have been reported.[15–17] However, these methods have limitations as they produce mainly N_1 substituted 1,2,3-triazole isomer but not N_2 substituted 1,2,3-triazole isomer. Many methods for the synthesis of N_2 substituted 1,2,3-triazole isomer have been reported in the past few years. The most important approaches are (i) Mitsunobu reaction of NH-triazoles with alcohols,[18] (ii) Cu(II)-catalyzed aerobic oxidation of bis arylhydrazones,[19] (iii) Ullman-type Cu(I)I-catalyzed amination of 1,2,3-triazole,[20] (iv) Chen's synthesis of *N*-2-aryl-1,2,3-triazole,[21] (v) from allylcarbonate, alkynes, and $TMSN_3$,[22] (vi) from chalcones and NaN_3 using Fe_2O_3 nanoparticles as catalyst,[23] (vii) regioselective *N*-2-substituted-1,2,3-triazoles with electrophiles,[24] (viii) *N*-2 selective palladium-catalyzed arylation of 1,2,3-triazoles,[25] (ix) from 2-arylhydrazononitriles and hydroxyl amine.[26] However, these methods have certain drawbacks as they involve tedious experimental procedures such as refluxing the reaction mixture at high temperature for long hours. It is, therefore, necessary to develop synthesis of N_2 substituted 1,2,3-triazole isomer at ambient temperature.

In recent years, copper(I) iodide has proved to be a very useful catalyst[27] in carrying out multicomponent synthesis of heterocycles such as triazoles,[28] benzoxazoles,[29] and pyrrolidines.[30] Copper(I) iodide has received increasing attention as an inexpensive, nontoxic, and readily available catalyst for organic synthesis. Copper(I) iodide has high tolerance to moisture as well as air, making it an ideal catalyst. It can be easily removed from the reaction mixture by quenching[31] and washing with water. The use of copper(I) iodide as a catalyst is not only cost-effective and regioselective and environmentally benign but also experimentally simple, easy to handle, and safe.[32]

Herein, we report the synthesis of N_1 and N_2 coumarin substituted 1,2,3-triazole isomers by the reaction of terminal alkynes, sodium azide, and 4-bromomethylcoumarins in the presence of copper(I) iodide as a catalyst and Et_3N as a base in one pot at ambient temperature under aerobic condition in good yields.

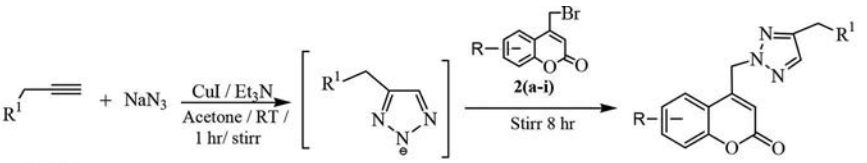
Results and discussion

4-Bromomethylcoumarins[33] **2(a–i)** were synthesized by Pechmann cyclization of substituted phenols with 4-bromoethylacetoacetate[34] using concentrated H_2SO_4 as a condensing agent. First the optimization of the reaction was studied, for which the reaction of 4-bromomethyl-6-methylcoumarin, sodium azide, and propargyl alcohol was selected as a model (Scheme 1). It is known that a copper(I) iodide in the presence of triethylamine catalyzed the one-step fusion of N_2 coumarin substituted 1,2,3-triazole by forming a better activated intermediate. A preliminary examination showed that copper(I) iodide in the presence of triethylamine in acetone among several solvents catalyzed the model reaction at room temperature. Of the reactions using different quantities of reactant, the best results were obtained by using a 1.2:1.0:1.0 ratio of sodium azide, propargyl alcohol, and 4-bromomethyl-6-methylcoumarin.

A mixture of sodium azide, propargyl alcohol, copper(I) iodide, and triethylamine in acetone was stirred for an hour at room temperature. 4-Bromomethyl-6-methylcoumarin was added and the stirring was continued for another 8 h. 4-((4-(Hydroxymethyl)-2*H*-1,2,3-triazol-2-yl)methyl)-6-methyl-2*H*-chromen-2-one **(3a)** was obtained in excellent yield (96%). If 4-bromomethyl-6-methylcoumarin was taken first, followed by adding sodium azide and alkyne, then N_1 coumarin substituted 1,2,3-triazole **(5a)** would be the product[35] (Scheme 2).

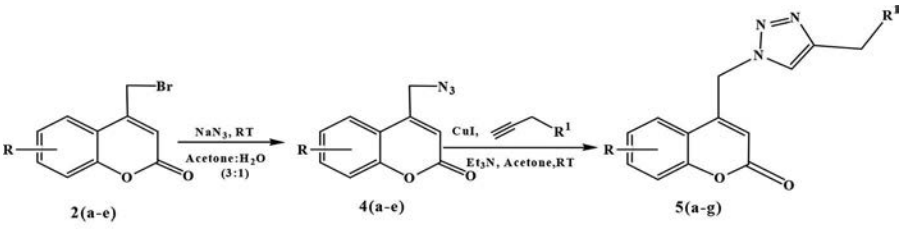
Decreasing the amount of catalyst from 10 mol% to 5 mol% lowered the N_2 coumarin substituted 1,2,3-triazole yield (65%) while increasing the amount of catalyst from 10 mol% to 20 mol% did not shown any significant impact on the N_2 coumarin substituted 1,2,3-triazole yield, indicating that this reaction condition was suitable for the one-pot assembly.

The role of solvents on the synthesis of N_2 coumarin substituted 1,2,3-triazole **(3a)** was then studied and the results are depicted in Table 1. Replacing the acetone by



compound	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	3k	3l
R	6-CH_3	6-MeO	6-Ethyl	6-*tert*-Butyl	6,8-Di methyl	7-CH_3	6-ipr	6-Cl	6-Br	6-CH_3	6-MeO	6-*tert*-Butyl
R^1	OH	OH	OH	OH	OH	OH	OH	OH	OH	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$

Scheme 1. Synthesis of N_2 coumarin substituted 1,2,3-triazoles.



Compound	5a	5b	5c	5d	5e	5f	5g
R	6-CH_3	6-Ethyl	6-ipr	6-*tert*-Butyl	6,8-Dimethyl	6-Ethyl	6,8-Dimethyl
R^1	OH	OH	OH	OH	OH	$N(CH_3)_2$	$N(CH_3)_2$

Scheme 2. Synthesis of N_1 coumarin substituted 1,2,3-triazoles.

acetonitrile produced the model in an appreciable yield (entry 3), albeit less than that produced by the former (entry 4). Other solvents such as ethanol, $CHCl_3$, dimethylformamide (DMF), and dimethylsulfoxide (DMSO) accomplished the model in moderate yields (56–72%, entries 1, 2, 5, and 6), while aqueous solvents including mixture of water with acetone, acetonitrile, and DMSO produced still lower yields (34–48%, entries 7, 8, and 9).

Optimized condition was established in acetone as a solvent system at room temperature for 9 h. This remarkable activation in reaction rate prompted us to explore the potential of this protocol for the synthesis of a variety of N_2 coumarin substituted 1,2,3-triazoles. All the aforementioned reactions proceeded expeditiously and delivered better to excellent product yields. The overall yield ranged from 96% of 4-((4-(hydroxymethyl)-2*H*-1,2,3-triazol-2-yl)methyl)-6-methyl-2*H*-chromen-2-one **(3a)** to 85% of 6-chloro-4-((4-(hydroxymethyl)-2*H*-1,2,3-triazol-2-yl)methyl)-2*H*-chromen-2-one **(3i)**.

A probable mechanistic pathway for the formation of N_2 coumarin substituted 1,2,3-triazoles is outlined (Fig. 2), which is in analogy to the established mechanism as reported in the literature.[36] The copper(I) species formed a pi complex with the triple bond of a terminal alkynes. In the presence of a base, the terminal hydrogen, being the most acidic, is deprotonated first to give a copper acetylide intermediate. Subsequent 1,3-dipolar cycloaddition with sodium azide produced 1,2,3-triazole anions that attacked 4-bromomethylcoumarins to give N_2 coumarin substituted 1,2,3-triazoles.

Table 1. Optimization of solvents at room temperature for the synthesis **(3a)**.

Entry	Solvent	Time (h)	Yield (%)
1	Ethanol	9	72
2	Chloroform	10	56
3	Acetonitrile	8	83
4	**Acetone**	**9**	**96**
5	DMF	10	60
6	DMSO	10	65
7	Acetone/H_2O (1:1)	11	48
8	Acetonitrile/H_2O (1:1)	11	34
9	DMSO/H_2O (1:1)	12	42

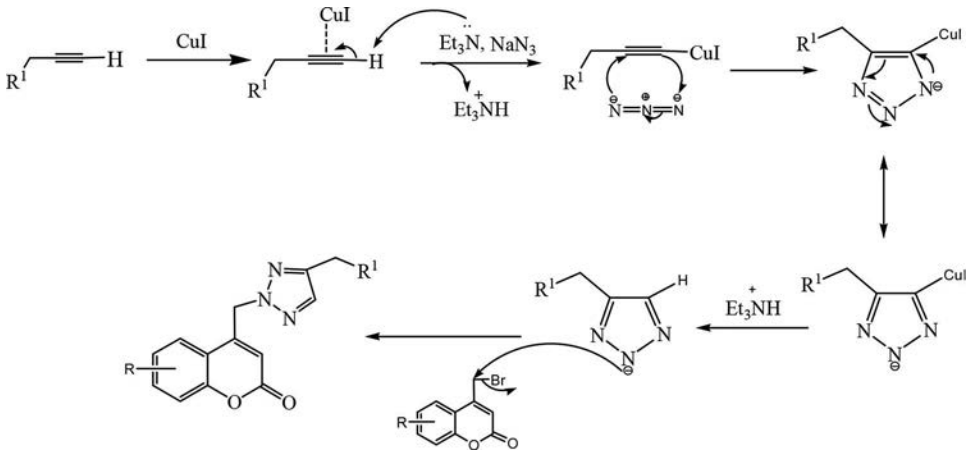


Figure 2. Plausible reaction mechanism for the *synthesis of* N_2 coumarin substituted 1,2,3-triazoles.

Conclusion

In conclusion, we have developed a simple and one-pot procedure for the synthesis of N_1 and N_2 coumarin substituted 1,2,3-triazole isomers from terminal alkynes, sodium azide, and 4-bromomethylcoumarins in the presence of copper(I) iodide as a catalyst and triethylamine as a base at ambient temperature in the aerobic condition in encouraging yields.

Experimental

The melting points were determined by open capillary method using an electric melting-point apparatus and are uncorrected. The IR spectra (KBr disc) were recorded on a Shimadzu-8400S FT-IR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker spectrometer by using $CDCl_3$/DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. The chemical shifts are expressed in δ parts per million (ppm). The high-resolution mass spectrum (HRMS) was recorded at IISC, Bangalore. The purity of the compound was checked by thin-layer chromatography (TLC). The elemental analyses were carried out using Elemental Vario Micro Cube CHN rapid analyzer. All the compounds gave satisfactory elemental analysis. The molecular structure of the compounds **3g** and **5d** are established by single-crystal x-ray analysis[37,38] (Figs. 3 and 4).

General procedure for the synthesis of 4-((4-(hydroxymethyl)-2H-1,2,3-triazol-2-yl)methyl)-6-methyl-2H-chromen-2-one (3a)

A mixture of propargyl alcohol (0.11 g, 1.9 mmol), sodium azide (0.14 g, 2.0 mmol), copper (I) iodide (10 mol%), and triethylamine (0.19 g, 1.9 mmol) in 20 ml of acetone was taken in a round-bottom flask and stirred for an hour. To this, 4-bromomethyl-6-methylcoumarin (0.5 g, 1.9 mmol) was added, and the stirring was continued for 8 h (the reaction was monitored by TLC). After the completion of the reaction, the catalyst was filtered through celite and the product was extracted with ether (3 × 10 ml). The solvent was removed under vacuum. The crude product was dried and recrystallized from ethyl acetate.

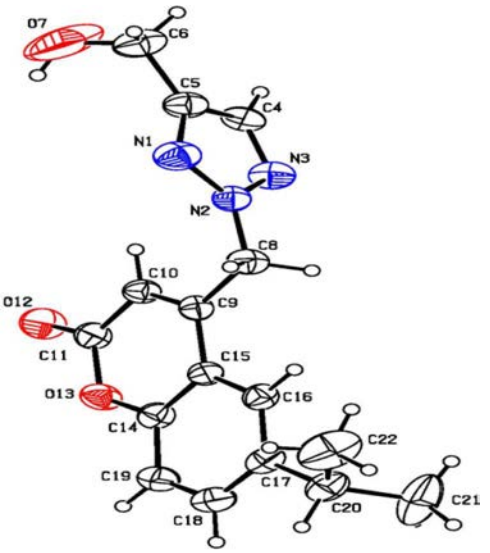


Figure 3. ORTEP diagram of the molecule **3g** at 40% probability.

4-((4-(Hydroxymethyl)-2H-1,2,3-triazol-2-yl)methyl)-6-methyl-2H-chromen-2-one (3a)

Yield 96%; colorless solid; mp 188–191 °C; IR (KBr, cm^{-1}): 1772 cm^{-1}(lactone C=O), 3238 cm^{-1}(OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 1H, OH), 2.42 (s, 3H, C_6-CH_3) 4.85 (s, 2H, -CH_2O-), 5.72 (s, 2H, -CH_2N-), 5.99 (s, 1H, C_3-H), 7.29 (m, 1H, C_7-H), 7.39 (m, 2H, C_8-H & C_5-H), 7.61 (s, 1H, Tr-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.4, 48.9, 55.0, 113.3, 116.5, 123.8, 124.6, 133.3, 133.8, 148.6, 149.7, 150.4, 151.1, 159.0 ppm. Anal. calcd. for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.94; H, 4.80; N, 15.43.

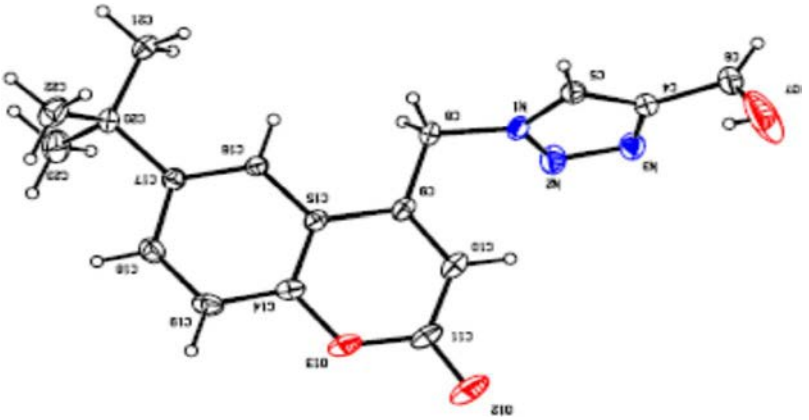


Figure 4. ORTEP diagram of the molecule **5d** at 50% probability.

General procedure for the synthesis of 4-(azidomethyl)-6-ethyl-2H-chromen-2-one (4b)[39,40]

4-Bromomethyl-6-ethylcoumarin (0.5 g, 0.001 mol) was taken in 15 ml acetone in a round-bottomed flask. To this, sodium azide (0.12 g, 0.001 mol) in 5 ml of water was added dropwise with stirring, which was continued for 3 h (the reaction was monitored by TLC). The reaction mixture was poured into ice-cold water, and the separated solid was filtered and recrystallized from ethyl acetate.

4-(Azidomethyl)-6-ethyl-2H-chromen-2-one (4b)

Yield 88%; colorless solid; mp 105–107 °C; IR (KBr, cm^{-1}): 1719 cm^{-1}(lactone C=O), 2120 cm^{-1}(N_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, 3H, CH_3 of C_2H_5 group, $J_{1,2} = 7.6$ Hz), 2.68 (q, 2H, CH_2 of C_2H_5 group, $J_{1,2} = 7.6$ Hz), 4.73 (s, 2H, -CH_2N-), 6.28 (s, 1H, C_3-H), 7.30 (d, 1H, C_7-H, $J_{1,2} = 8.4$ Hz), 7.35 (d, 1H, C_8-H, $J_{1,2} = 8.4$ Hz), 7.40 (s, 1H, C_5-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.9, 25.6, 53.2, 113.3, 116.3, 121.0, 123.5, 133.6, 134.7, 148.6, 150.3, 160.8 ppm. Anal. calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.79; H, 4.71; N, 18.23.

General procedure for the synthesis of 4-((4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)methyl)-6-methyl-2H-chromen-2-one (5a)

To a solution of propargyl alcohol (0.11 g, 1.9 mmol) in acetone, CuI (10 mol%) and triethylamine (0.19 g, 1.9 mmol) were added. The mixture was stirred at room temperature for 15 min. Then, 4-(azidomethyl)-6-methyl-2H-chromen-2-one (0.42 g, 1.9 mmol) was added and resulting mixture was stirred until the starting material was consumed as judged by TLC. After the completion of the reaction, the catalyst was filtered through celite and the product was extracted with ether (3 × 10 ml). The solvent was removed under vacuum. The crude product was dried and recrystallized from ethyl acetate.

4-((4-(Hydroxymethyl)-1H-1,2,3-triazol-1-yl)methyl)-6-methyl-2H-chromen-2-one (5a)

Yield 90%; colorless solid; mp 224–226 °C; IR (KBr, cm^{-1}): 1714 cm^{-1}(lactone C=O), 3228 cm^{-1}(OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (s, 1H, OH), 2.45 (s, 3H, C_6-CH_3) 5.08 (s, 2H, -CH_2O-), 5.92 (s, 2H, -CH_2N-), 6.19 (s, 1H, C_3-H), 7.29–7.44 (m, 3H, Ar-H), 8.23 (s, 1H, Tr-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.3, 50.8, 56.7, 104.5, 112.6, 114.5, 116.6, 117.0, 119.6, 129.9, 147.6, 148.7, 151.8, 160.4 ppm. Anal. calcd. for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.95; H, 4.80; N, 15.39.

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